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AMINO-FUNCTIONALIZED $CoFe_2O_4$ MAGNETIC NANOPARTICLES AS AN EFFICIENT HETEROGENEOUS CATALYST FOR BENZALDEHYDE CYANOSILYLATION

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SUMMARY

Diaminosilane-functionalized cobalt spinel ferrite ($CoFe_2O_4$) magnetic nanoparticles were synthesized and used as an efficient heterogeneous base catalyst for the cyanosilylation reaction benzaldehyde with trimethylsilyl cyanide. The magnetic nanoparticle catalyst was characterized by X-ray powder diffraction (XRD), transmission electron microscope (TEM), thermogravimetric analysis (TGA), fourier transform infrared (FT-IR), nitrogen physisorption measurements. Quantitative conversion (>99%) was achieved under mild conditions. Recovery of catalyst was facilely achieved by magnetic decantation. The supported catalyst could be reused without significant degradation in catalytic activity.

I - INTRODUCTION

The immobilization of homogeneous catalysts to facilitate easy catalyst recovery and recycling as well as product separation is a longstanding pursuit of catalysis science [1]. Various support matrices such as organic polymers and inorganic silica, especially porous inorganic materials with high surface areas, have been employed [2]. Nanoparticles have emerged as efficient alternative support materials for homogeneous catalyst immobilization [3]. However, in this case, facile separation and recycling of nanoparticle materials from reaction media still remains a challenge. This issue can be addressed by using magnetic supports, allowing the catalyst to be easily separated from the liquid reaction media with application of an external magnetic field [4]. In the field of catalysis, magnetic nanoparticles have been utilized as catalyst supports for organic transformations such as olefin hydroformylation [5], nitrobenzene hydrogenation [6], olefin hydrogenation [7], Suzuki cross-coupling reaction [8], and asymmetric hydrogenation [9], as well as supports for biocatalysts [10].

The cyanosilylation reaction of aromatic aldehydes with trimethyl cyanide has been considered as one of the most powerful procedures for the synthesis of polyfunctionalized molecules [11]. A variety of Lewis acids and Lewis bases have been employed successfully as promoters in cyanosilylation of aldehydes and ketones [12]. However, the number of methods for effecting catalytic cyanosilylation of aldehydes and ketones remains quite limited. We recently demonstrated the utilization of diamine-functionalized superparamagnetic spinel ferrite nanoparticles as efficient heterogeneous catalyst for low temperature liquid phase reactions, in which the Knoevenagel reaction of malanonitrile with benzaldehyde was utilized as

a well-known model reaction under very mild conditions [13]. In this work, we wish to report the first example of cyanosilylation reaction of benzaldehyde using the diamine-functionalized superparamagnetic spinel ferrite nanoparticles as a catalyt.

II - EXPERIMENT

1. Materials and instrumentation

Chemicals were purchased from Aldrich, Alfa Aesar, and Acros and used as received without further purification. A Fischer Scientific FS60H was used to sonicate samples. Nitrogen physisorption measurements were conducted using a Micromeritics ASAP 2010 system. The surface areas were analyzed by the BET method. A Netzsch Thermoanalyzer STA 409 was used for simultaneous thermal analysis combining thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10ºC/min in air.

X-ray powder diffraction (XRD) patterns were recorded using Cu Kα radiation source on a Scintag X1 powder diffractometer. Transmission electron microscopy studies were performed using a JEOL 100CX II Transmission Electron Microscope (TEM) at 100 kV and 100,000 magnifications. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker IFS 66 V/S instrument with samples being dispersed on potassium bromide pallets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 14-A equipped with a flame ionization detector (FID) and an HP-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis heated samples from 50 to 140ºC at 30ºC/min, from 140 to 300ºC at 40ºC/min, and held at 300ºC for 2 min. *p*-Xylene was used as an internal standard to calculate reaction conversion. GC-MS analyses were performed using a Hewlett Packard GC-MS 5890.

2. Synthesis of amino-functionalized magnetic nanoparticles

Cobalt spinel ferrite ($CoFe_2O_4$) nanoparticles were synthesized following a microemulsion method [14, 15]. $CoFe_2O_4$ nanoparticles (1.1 g) were dispersed in a mixture of ethanol and water (150 ml, 1:1 by volume). Ammonium hydroxide (15 ml, 29% v/v aqueous solution) was added, and the mixture was stirred vigorously at 60ºC for 24 hr under an argon atmosphere. The nanoparticles were washed with copious amounts of deionized water, ethanol, and hexanes via magnetic decantation. The resulting product was redispersed in a mixture of ethanol and water (150 ml, 1:1 by volume), and sonicated for 30 min at room temperature. *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (1g) was then added, and the solution was heated at 60ºC with vigorous stirring for 24 h under an argon atmosphere. The final product was washed with copious amounts of deionized water, ethanol, and hexanes by magnetic decantation, and dried under vacuum at room temperature overnight to yield amino-functionalized magnetic nanoparticles (1.1 g).

3. Catalytic studies

Unless otherwise stated, a mixture of basic magnetic nanoparticles (33 mg, 2.5 mol%), benzaldehyde (40 mg, 0.38 mmol), and p-xylene (21 mg, 0.2 mmol) in toluene (3 ml) was placed into a 10 mL glass vessel. The reaction vessel was sonicated for 5 minutes at room temperature. A solution of trimethylsilyl cyanide (56 mg, 0.57 mmol) in toluene (1 ml) was then added, and the resulting mixture was stirred at room temperature under an argon atmosphere. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with acetone, filtering through a short silica gel pad, analyzing by GC with reference to *p*-xylene, and further confirming product identity by GC-MS.

III - RESULTS AND DISCUSSION

1. Catalyst synthesis and characterization

Cobalt spinel ferrite ($CoFe_2O_4$) nanoparticles were synthesized following a microemulsion

method [14]. It was previously reported that magnetic nanoparticles synthesized in basic aqueous media are covered with a number of hydroxyl (-OH) groups, due to the adsorption of hydroxyl groups and protons (H^+) on the bare atoms of the metal and oxygen, respectively [16]. The hydroxyl groups on the surface of the magnetic nanoparticles were then enriched with an aqueous solution of ammonia, facilitating the surface modification step. The resulting nanoparticles were functionalized with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine to create surface base sites, according to a slightly modified literature procedure [15] (figure 1). It was decided to immobilize diamine species on the nanoparticle surface as the diamine previously exhibited high activity in base-catalyzed reactions under mild conditions [17].

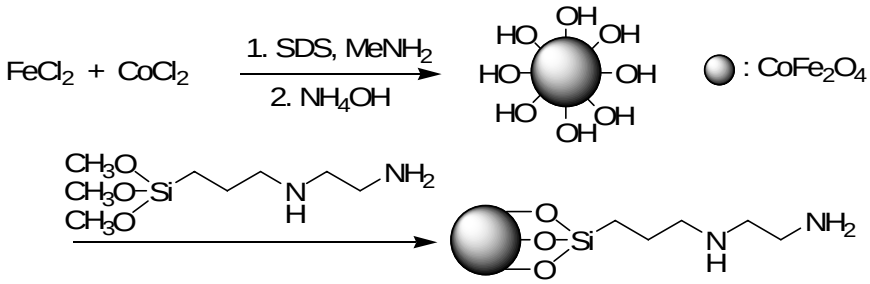

Figure 1: Scheme of preparation and functionalization of magnetic nanoparticles

The amino-functionalized super-paramagnetic nanoparticles were characterized using a variety of different techniques. X-ray powder diffraction (XRD) showed that the magnetic nanoparticles are $CoFe_2O_4$ spinel ferrites, with XRD patterns being consistent with literature [14] (figure 2). No impurity peak was observed in the XRD diffractogram. Thermogravimetric analysis (TGA) of the supported catalyst showed that approximately 0.3 mmol/g of the diamine was immobilized on the ferrite nanoparticles.

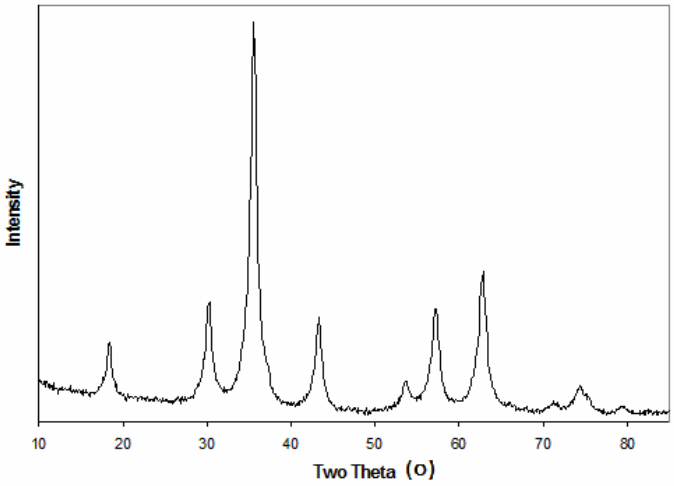

Figure 2: X-ray powder diffractogram of the functionalized magnetic nanoparticles

Transmission electron microscopy (TEM) studies showed an average diameter of approximately 30 nm for the particles (figure 3). Particle agglomeration was clearly observed for the unmodified nanoparticles, and the primary particle size is likely closer to 10 nm in

diameter. A slight agglomeration was also observed for the amino-functionalized ferrite nanoparticles, though it was much less pronounced. It was inferred that the electrostatic interaction between amino groups of the silane coated on the surfaces reduces the aggregation of the ferrite nanoparticles. This is in good agreement with the observations of Liang et al. [15], where magnetite nanoparticles (Fe_3O_4) were coated with 3-aminopropyltriethoxysilane. It should be noted that most oxide particles, regardless of composition, aggregate on TEM grids and the images do not imply that the nanoparticles aggregate similarly in solution.

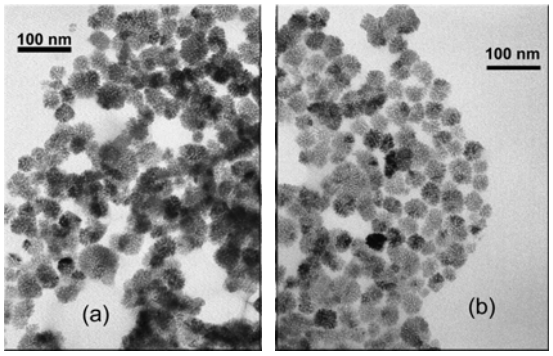

Figure 3: TEM micrograph of the unfunctionalized (a) and amino-functionalized (b) magnetic nanoparticles

Nitrogen physisorption measurements of the nanoparticles gave BET surface areas of 200 m^2/g and no measurable mesoporosity. Fourier transform infrared (FT-IR) spectra of both the unfunctionalized and amino-functionalized nanoparticles showed the presence of an Fe-O stretching vibration at approximately 595 cm^{-1}, an O-H stretching vibration due to physisorbed water and potentially surface hydroxyls near 3420 cm^{-1}, and an O-H deformation vibration near 1630 cm^{-1}, respectively (figure 4). The significant features observed for the diamine-functionalized nanoparticles are the appearance of the peaks at 1017 cm^{-1} (Si-O stretching), and 2920 cm^{-1} (-CH_2 stretching). There also exists the contribution of the -NH_2 group for the band near 3300 cm^{-1}, which is overlapped by the O-H stretching vibration. These features revealed the existence of the aminosilane species on the particles, and the spectrum is in good agreement with literature [15, 16].

2. Catalytic studies

The magnetic nanoparticle-supported diamine catalyst was assessed for its activity in the cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide to the corresponding cyanohydrin trimethylsilyl ether as the principal product [11, 12] (figure 5). The initial reaction was carried out using 0.5 mol% magnetic catalyst relative to benzaldehyde in toluene at reflux temperature. Complete conversion was achieved within just 5 minutes with no trace amount of benzaldehyde being detected by GC. It was therefore decided to carry out the reaction under milder conditions (i.e. room temperature).

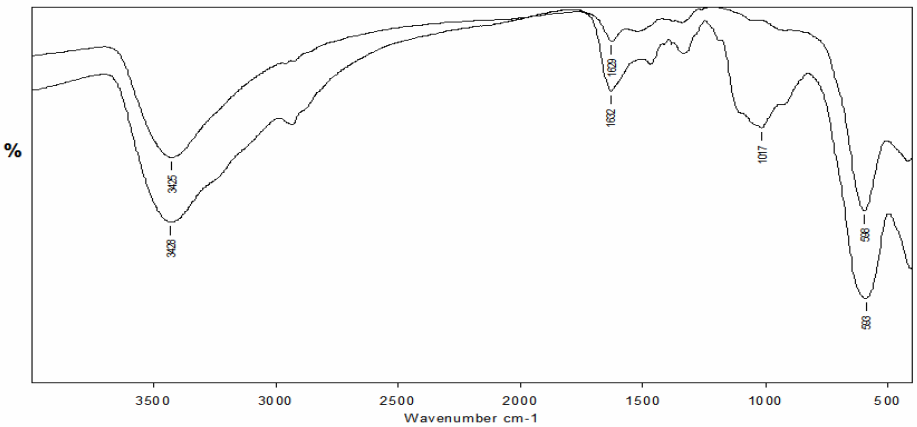

Figure 4: FT-IR spectra of unfunctionalized (top) and amino-functionalized (bottom) magnetic nanoparticles

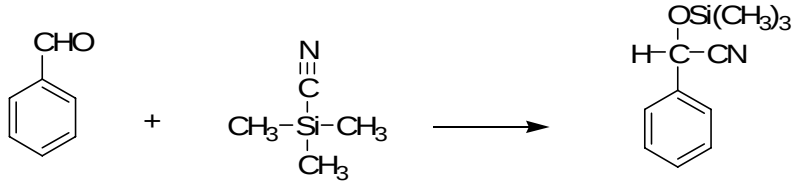

Figure 5: Scheme of the cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide

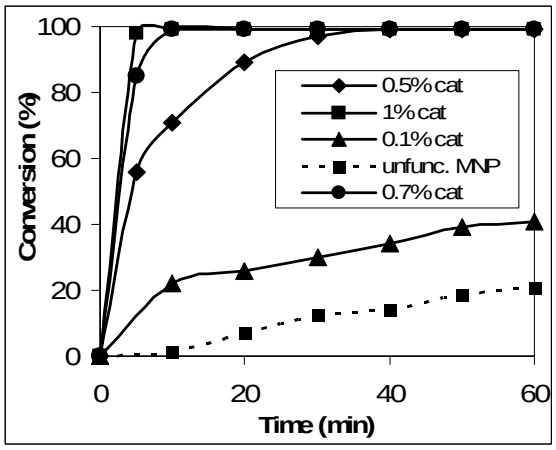

Figure 6: Effect of catalyst concentration on reaction conversion

The catalyst concentration, with respect to the diamine moiety immobilized on the magnetic nanoparticles, was studied in the range of 0.1 - 1 mol% at room temperature. Aliquots were withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction. Experimental results are summarized in figure 6. Quantitative conversion (> 99%) of benzaldehyde was achieved in just 5 minutes at 1 mol% catalyst loading. As expected, decreasing the catalyst loading resulted in a drop in reaction rate, with complete conversion being observed within 10 minutes at 0.7 mol% catalyst loading. Reaction using 0.5 mol% catalyst afforded a conversion of 99% within 40 minutes. However, a conversion of only 41% was observed after 60 minutes for the reaction using 0.1 mol% catalysts loading. The results indicated that the diamine-functionalized magnetic nanoparticles were quite active in cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide. It should be noted that the unfunctionalized magnetic nanoparticles were also slightly active in the reaction, with with approximately 20% conversion being observed after 60 minutes.

The performance of the magnetic base catalyst in the cyanosilylation reaction was then directly compared with commercial diamine-functionalized silica gel and resin catalysts. The diamine moiety immobilized on the silical gel and the resin was identical to the magnetic nanoparticles. The particle size of the silica catalyst was 40 - 60 μm and the particle size of the resin catalyst was 150 - 200 μm. The reactions using these commercial catalysts were carried out under identical conditions as compared to the basic magnetic nanoparticle-catalyzed reaction. At the catalyst loading of 0.5 mol%, the silical catalyst was only very weakly active in the cyanosilylation reaction with approximately 10% conversion being achieved after 60 minutes, while the activity of the resin catalyst was almost negligible. Increasing the catalyst loading up to 5% only afforded 40% conversion for the silica-catalyzed reaction and 10% conversion for the resin-catalyzed reaction, respectively (figure 7). The results indicated that the basic magnetic nanoparticles exhibited superior activity in the cyanosilylation reaction, as compared to the commercial silica and resin catalysts.

The sensitivity of a heterogeneously catalyzed reaction to different solvents can usually be of extreme importance, depending on the nature of the catalyst support material. We therefore decided to investigate the solvent effect in the basic magnetic nanoparticle-catalyzed reaction, using 0.5 mol% catalyst loading at room temperature. In this work, a combination of toluene and the basic magnetic catalyst afforded excellent conversions for the reaction within a short reaction time (figure 8). The reaction carried out in *n*-hexane, a relatively

more non-polar solvent, gave a higher reaction rate with all of the benzaldehyde being converted to the desired product within 10 minutes. Interestingly, the basic magnetic catalyst was also very reactive in ethyl acetate, a more polar solvent than toluene. The reaction using dichloromethane (DCM) also afforded a complete conversion although a slight drop in reaction rate was observed, compared to the reaction in toluene (figure 8). However, it was observed that acetonitrile was not suitable for the reaction as the reaction stopped at the conversion of approximately 85%. It was previously proposed that the rate of the reaction of benzaldehyde and malononitrile using silica-based catalysts was influenced by the partitioning of the reactants (polar) between the catalyst pores and/or surface (polar) and the bulk reaction media (i.e. partitioning away from the catalyst pores/surface was increased with more polar solvents) [18, 19]. The similar trend in the effect of solvent polarity (i.e. non-polar solvents are advantageous) observed for the magnetic nanoparticle catalyst in this study may be rationalized based on the same reasons. However, the problem still needs further studies.

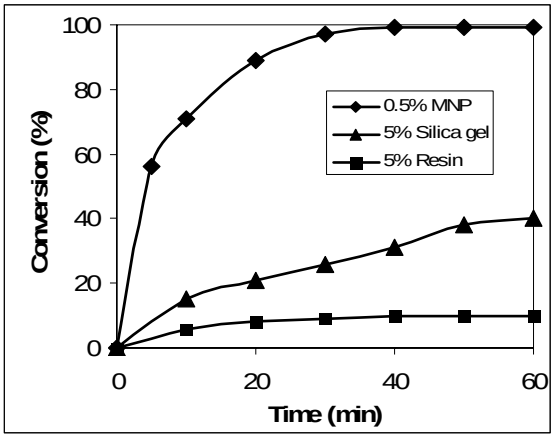

Figure 7: Effect of catalyst support material

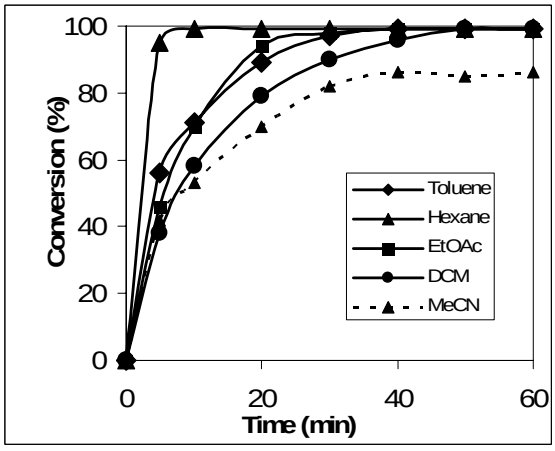

Figure 8: Effect of solvent on reaction conversion

One point of great concern for most of anchored catalysts is the ease of separation as well as the deactivation and reusability of the catalyst. The basic magnetic nanoparticle catalyst was therefore investigated for recoverability and reusability in the cyanosilylation reaction. The reaction was carried out in toluene at room temperature using 0.5 mol% catalyst loading in 60 minutes. To separate the catalyst, an external magnetic field was applied on the outer surface of the glass reaction vessel containing the magnetic nanoparticles using a small permanent magnet. The reaction solution was then easily removed from the reaction vessel by decantation while the external magnet held the basic nanoparticles stationary inside the vessel. The magnetic catalyst was washed with toluene to remove any physisorbed reagents, dried under vacuum at room temperature overnight, and reused in a second run under identical conditions to the first run. Quantitative conversion (> 99%) was still achieved, with all of the benzaldehyde being converted to the desired product. Although kinetic data were not taken for the catalyst recycling study, it was obvious that the catalyst could be resued without significant degradation in activity.

IV - CONCLUSIONS

In conclusion, cobalt spinel ferrite ($CoFe_2O_4$) magnetic nanoparticles were readily synthesized and functionalized with damine moiety via silane chemistry to create surface basic sites. The basic magnetic nanoparticles

were used as an efficient heterogeneous catalyst for the cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide under mild conditions. The basic magnetic nanoparticle catalyst exhibited superior activity in the reaction, as compared to commercial silica and resin catalysts. More importantly, the basic magnetic catalyst could be facilely isolated from the reaction mixture by simple magnetic decantation using a permanent magnet. The magnetic supported catalyst could be reused without significant degradation in activity. Our results here demonstrate the feasibility of applying magnetic nanoparticles as catalyst supports for immobilizing homogeneous catalysts. The unique properties of the particles such as nanometer-sized, magnetic, and facilely functionalized via silane chemistry, offer potential advantages over conventional catalyst support materials, and would be interested to the chemical industry.

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